Notes

Influence of a Nonionic Surfactant on the Dilute Hydrodynamical Properties of a Hydrophobically Associating Water Soluble Polymer

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Introduction

Hydrophobically associating polymers form a class of commercial products present in many industrial applications and mainly used as thickeners and, generally speaking, as rheology modifiers.[1,2] These polymers are composed of a hydrophilic skeleton and a small number of hydrophobic substituents, in the form of pendant side chains or terminal groups. Their pecular linear and nonlinear rheological behaviors are due to the formation of an intermolecular hydrophobic association network above a certain polymer concentration, as studied experimentally,[3–6] theoretically,[7] and numerically.[8]

The addition of nonionic surfactant molecules, present in a number of industrial formulations, has been shown to significantly modify the rheological properties of hydrophobically associating polymers in the semidilute and concentrated regime, where the hydrophobic interaction network exists.[9–12] The aim of the present paper is to study the effect of the presence of a nonionic surfactant on the dilute hydrodynamical properties of a hydrophobically associating water soluble polymer, namely (hydroxypropyl)guar. This contributes to a better understanding of hydrophobically associating polymer/surfactant interactions and their hydrodynamical effects.

Experimental Section

The polymers used for this study have all been supplied by Lamberti spa (Albizzate, Italy). They are of two types:

(1) The precursor is (hydroxypropyl)guar containing an average of one hydrophilic substituent (hydroxypropyl group) per monomer. The average molecular weight is $M_w = 1.8 \times 10^6$, corresponding to a degree of polymerization of about 3000, and the dispersity index is about 1.5.[13] Like guar gum, the native polymer, (hydroxypropyl)guar is a slightly stiffened random-coil chain.[14] The structure of the repeating unit of guar and (hydroxypropyl)guar is shown in Figure 1.

(2) The hydrophobically modified (hydroxypropyl)guar is obtained by reaction of (hydroxypropyl)guar with a 1.2% of mixture C_{22}–C_{28} *n*-alkyl epoxides. The average number of

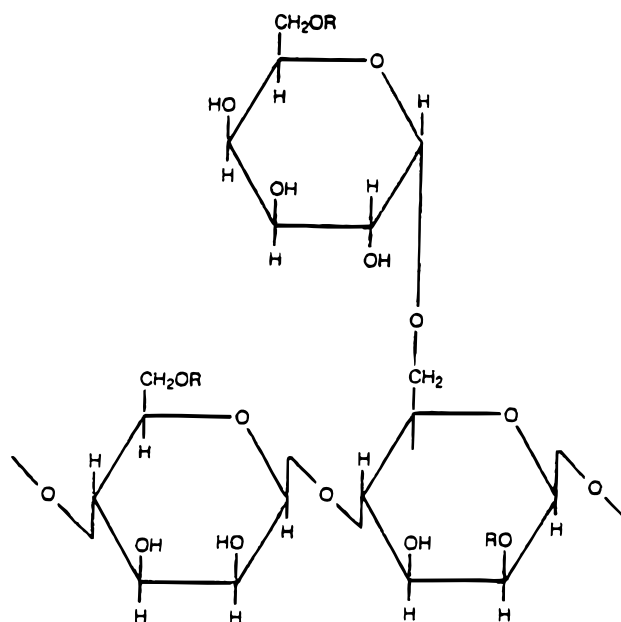* To whom correspondence should be addressed.

Figure 1. Structure of the repeating unit of guar (R = H) and (hydroxypropyl)guar (R = $CH_2CH_2CH_2OH$).

hydrophobic substituents per polymer chain lies between 0 and 10,[15] and the hydrophobic substitution has been shown to lead to hardly no chain degradation of the precursor.[13]

The dilute hydrodynamical properties of (hydroxypropyl)-guar and hydrophobically modified (hydroxypropyl)guar have been measured and we have shown that the intrinsic viscosity of both polymers in water was the same, 1050 cm³/g; this somewhat surprising result may be explained by the very low degree of hydrophobic alkylation of the chains: the very few potential intramolecular hydrophobic associations per macromolecule are not efficient enough to lead to a significant collapsed conformation of the chains, whereas the Huggins coefficient is more influenced by the hydrophobic modification: it has a value of 0.8 for the precursor and a value of 1.1 for the hydrophobically modified polymer, indicating a significant tendency to intermolecular association once intermolecular interactions appear.

• The surfactant used in this work is a polyoxyethylated octylphenol with an average of 9–10 units of ethylene oxide, commercialized by Union Carbide as Triton X-100. The critical micelle concentration of Triton X-100 has been determined from surface tension measurements; the value obtained, 2×10^{-4} mol L^{-1}, is in very good agreement with literature data.[16]

All polymer/surfactant solutions were prepared in freshly distilled water and tested just after preparation. All viscometric measurements have been carried out at 25 ± 0.1 °C on a Contraves Low-Shear 30 viscometer equipped with a Couette geometry, characterized by an inner cylinder diameter of 1.102 cm, an outer cylinder diameter of 1.198 cm, and a cylinder height of 8 mm.

Reproducibility has been studied systematically and relative errors on viscosity values have been shown to be less than 5%.

Results

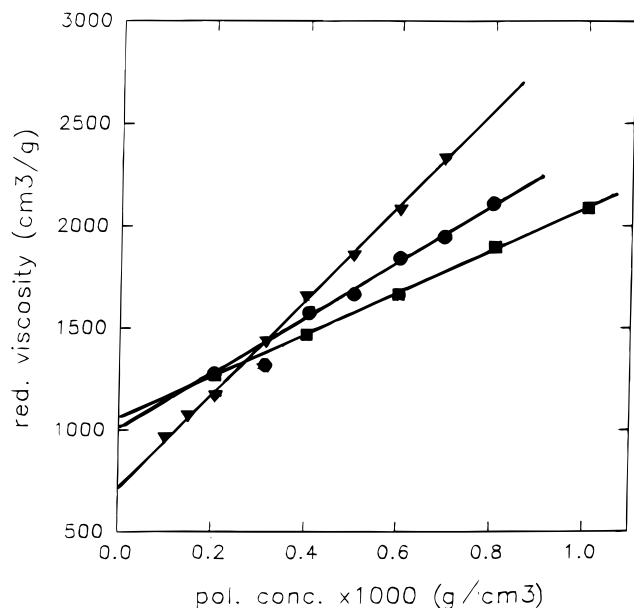Reduced steady shear viscosity of hydrophobically modified (hydroxypropyl)guar as a function of polymer

Figure 2. Reduced viscosity as a function of polymer concentration for hydrophobically modified (hydroxypropyl)guar solutions, at three surfactant concentrations: 5×10^{-5} mol/L (●); 2.5×10^{-4} mol/L (▼); 10^{-2} mol/L (■).
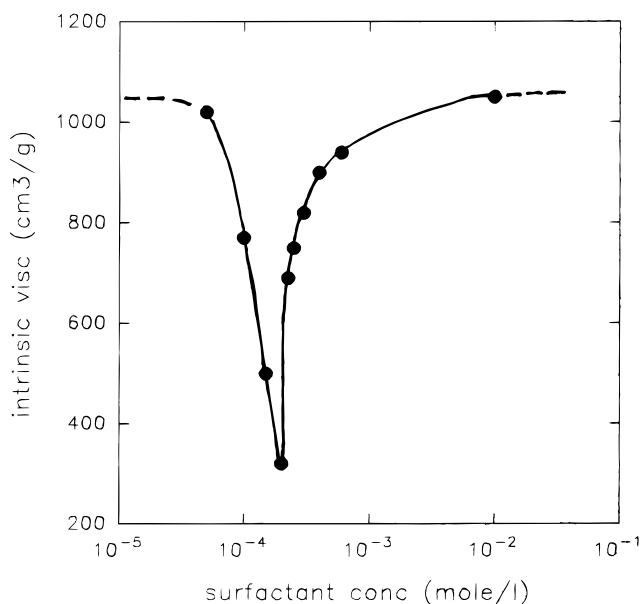

Figure 3. Intrinsic viscosity as a function of surfactant concentration for hydrophobically modified (hydroxypropyl)guar solutions.

concentration *c* for different surfactant concentrations is shown in Figure 2. The plots have a good linearity, which allows a satisfactory determination of intrinsic viscosity $[\eta]$ and Huggins coefficient K_H, obtained using the Huggins equation

$$\eta_{sp}/c = [\eta] + K_H[\eta]^2\, c + \dots \qquad (1)$$

where $\eta_{sp} = \eta_r - 1$ is the specific viscosity and η_r, the ratio of the solution to solvent viscosities, is the relative viscosity; η_{sp}/c is the reduced viscosity.

Figures 3 and 4, respectively, show the intrinsic viscosity and Huggins coefficient of hydrophobically modified (hydroxypropyl)guar as a function of surfactant concentration.
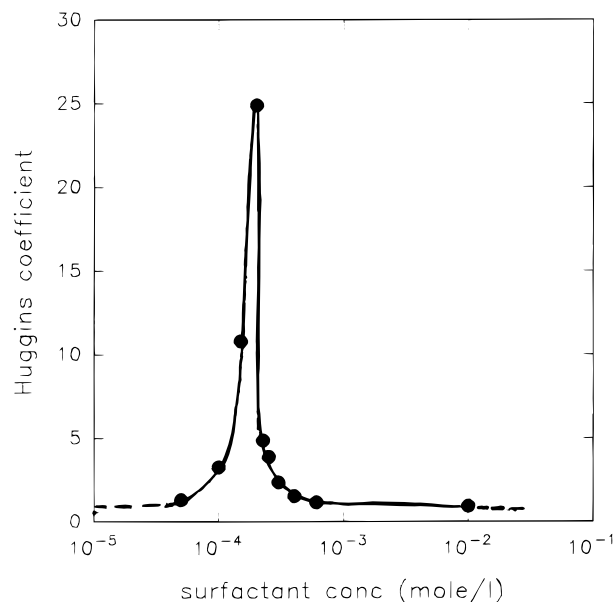
Two limit surfactant concentrations appear:

Figure 4. Huggins coefficient as a function of surfactant concentration for hydrophobically modified (hydroxypropyl)-guar solutions.

(1) At very low surfactant concentrations, the intrinsic viscosity and Huggins coefficient, respectively, tend to 1050 cm³/g and 1.1, which are the values of intrinsic viscosity and Huggins coefficient obtained with hydrophobically modified (hydroxypropyl)guar alone in distilled water.

(2) At high surfactant concentrations, the intrinsic viscosity and Huggins coefficient tend to 1050 cm³/g and 0.8, respectively, which are the values of intrinsic viscosity and Huggins coefficient obtained with the precursor (hydroxypropyl)guar alone in distilled water.

Between these two limits, that is for surfactant concentrations that lie from 4×10^{-5} to 10^{-3} mol L^{-1}, (1) adding surfactant, up to its critical micelle concentration in water, leads to a sharp decrease of intrinsic viscosity and a sharp increase of Huggins coefficient and (2) further surfactant addition leads, on the contrary, to a sharp increase of intrinsic viscosity and a sharp decrease of Huggins coefficient.

Discussion

The surfactant concentration dependence of viscometric results in the polymer dilute regime can be discussed using the same arguments as those presented to explain the surfactant concentration dependence of rheological measurements carried out in the polymer semidilute and concentrated regime.[9,10]

• Below the critical micelle concentration of the pure surfactant in water, surfactant molecules interact with the hydrophobic groups and form mixed polymer/surfactant aggregates that strengthen the inter- or/and intramolecular hydrophobic junctions.This "strengthening" effect has two consequences:

At infinite polymer dilution, intramolecular hydrophobic associations prevail and surfactant addition leads to a more compact conformation of the hydrophobically modified macromolecules, and thus a decrease of the intrinsic viscosity with an increase of surfactant concentration.

At low polymer concentrations, intermolecular hydrophobic associations appear and surfactant addition leads

to an increase of the Huggins coefficient with an increase of surfactant concentration.

• Above the critical micelle concentration of the pure surfactant in water, surfactant micelles tend progressively to envelop and neutralize the hydrophobic groups and break the intra- or/and intermolecular hydrophobic junctions. This "weakening" effect has two manifestations:

At infinite dilution, surfactant addition leads to a progressive, and finally total, destruction of the intramolecular hydrophobic associations, as shown by the increase of the intrinsic viscosity with an increase of surfactant concentration.

At low polymer concentrations, surfactant addition leads to a progressive, and finally total, destruction of the intermolecular hydrophobic associations, as shown by the decrease of the Huggins coefficient with an increase of surfactant concentration.

Conclusion

The results reported in this paper show that the dilute hydrodynamic properties of hydrophobically modified polymers are strongly influenced by the presence of nonionic surfactant.

The critical micelle concentration of the pure surfactant in water corresponds to the maximum polymer/surfactant interaction effects:

• At infinite polymer dilution, the mixed polymer hydrophobic groups/surfactant aggregates form the most intense intramolecular hydrophobic associating junctions, as revealed by the minimum of intrinsic viscosity.

• At low polymer concentrations, the tendency to intermolecular hydrophobic associations is maximum, as shown by the maximum of Huggins coefficient.

References and Notes

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